

# Temperature-Yield Profiles of Tobacco and Tobacco Constituents

## II. Yields of Phenol and Cresols from Untreated and Borate-Treated Cellulose and Lignin\*

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### INTRODUCTION

In studies concerning the effect of chemical modifiers on the composition of cigarette smoke, it has been shown that certain of these modifiers substantially alter the levels of various smoke components (1).

In particular, it has been found that the smoke condensate from cigarettes made from tobacco which has been treated with 10% (w/w) of a mixture of boric acid-sodium tetraborate decahydrate (3:7) contains significantly greater amounts of phenol, o-cresol, and m,p-cresol. To gain some insight as to the general mode of action of this modifier, the temperature-yield profiles for various smoke components were obtained from the isothermal pyrolysis of untreated and borate-treated tobacco (2). These temperature-yield profiles have shown that for untreated tobacco there are two distinct modes of phenol formation. Addition of borate to the tobacco suppresses the phenol formation at lower temperatures and greatly enhances its formation at higher temperatures. An increase in the recovery of the cresols also was observed, but the temperatures at which the maximum recoveries occurred were not significantly altered by the addition of borate to the tobacco. This initial work did not, however, give any indication as to the effect of this modifier on specific leaf constituents.

The purpose of this study was to determine whether the enhancement of the phenol and cresol formation is due to the interaction of borate with a particular leaf constituent. This paper describes the influence of the addi-

tion of 10% (w/w) of a mixture of boric acid-sodium tetraborate decahydrate on the yields of phenol, o-cresol, and m,p-cresol obtained from the isothermal pyrolyses of cellulose and lignin.

### EXPERIMENTAL

The apparatus used for this study was the same as that previously described for obtaining the temperature-yield profiles for untreated and borate-treated tobacco (2). All pyrolyses were conducted in an atmosphere of air.

The cellulose used was purified wood cellulose (Solka-floc, Brown Company\*). Treatment with the borate mixture was accomplished by alternately spraying with a solution of the additive and drying as has been described for the treatment of tobacco (1). The lignin used was isolated from tobacco by a scale-up of the analytical procedure described for the determination of crude lignin (3). Salts were removed from the lignin by dialysis. Borate-treated lignin was prepared by evaporating a solution of boric acid-sodium tetraborate with the calculated amount of powdered lignin in a rotary evaporator. Both the cellulose and lignin were treated with 10% (w/w) level of  $H_3BO_3 \cdot Na_2B_4O_7 \cdot 10H_2O$  (3:7).

After the pyrolysis of a sample the reaction products were removed from the traps by alternate washings with 0.5N sodium hydroxide and cyclohexane. The cyclohexane solution was then thoroughly extracted with 0.5N sodium hydroxide to obtain the phenols. The analysis of the phenols was performed as has been previously described for the analysis of phenols from tobacco (4). Thermoanalytical data were obtained as previously described (5) and were all run in air.

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## RESULTS AND DISCUSSION

### 1. Phenol from Cellulose

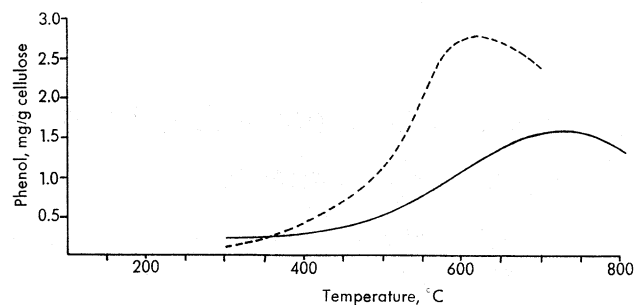
The temperature-yield profile for phenol from untreated cellulose is shown in Figure 1. It is seen that a small amount of phenol is formed at temperatures as low as 300° C. Phenol formation at 300° C is predictable since this is approximately 50° C higher than the onset of decomposition as shown by thermogravimetric analysis (see Figure 7). As shown in the temperature-yield profile, phenol recovery does not increase markedly until approximately 450° C. Above 450° C phenol recovery increases until a maximum is reached between 700° and 750° C. It has been reported that phenol is not formed from the pyrolysis of cellulose at temperatures below 400° C (6, 7). The use of smaller samples and the analytical methods employed in these studies could account for their not detecting the phenol formed at these lower temperatures. Kato et al. (8) have shown, however, that phenol was obtained in 0.2% yield from the bulk pyrolysis of a 100 gm sample of cellulose at 350° C. This is significantly higher than the yield obtained from this study. This higher yield can be attributed to the method of pyrolysis employed which allowed the reaction products to be held at the pyrolysis temperature for a longer period of time. Secondary reactions taking place during the extended reaction time will lead to the formation of more thermally stable products such as phenols.

The temperature-yield profile for phenol recovery from borate-treated cellulose also is shown in Figure 1. This profile is significantly different from that for the phenol recovery from untreated cellulose. Phenol recovery from borate-treated cellulose gradually increases from 300° C until it reaches a maximum between 600° and 650° C. This maximum is approximately 100° C lower than that from untreated cellulose and is similar to that observed for borate-treated tobacco (2). Not only is the temperature of maximum phenol recovery decreased, but there is also an approximate two-fold increase in the amount of phenol recovered. This increase in phenol recovery is approximately the same as that obtained from borate-treated tobacco.

The temperature-yield profile for phenol recovery from borate-treated tobacco differs significantly from that of the untreated tobacco (2). The profile for phenol recovery from the treated tobacco contains a single maximum at 500° C whereas the profile from untreated tobacco has two maxima which occur at approximately 300° and 600° C. Recovery of phenol from the treated tobacco at 500° C is approximately two times that from the untreated tobacco. This ratio of phenol recovery from borate-treated tobacco to untreated tobacco is very close to the 2.4:1 ratio obtained from the smoke condensates of cigarettes made from borate-treated tobacco and untreated tobacco (1).

The action of borate salts on the thermal decomposition of cellulose and the resulting increase in the level of phenol is too complex for a simple mechanistic approach. However, from other studies it is possible to postulate

Figure 1 Temperature-yield profile of phenol from cellulose  
Untreated — and borate-treated - - -



a gross mode of action of borate salts on the decomposition of cellulose with regard to the recovery of phenol and cresols. Based on studies of Madorsky et al. (9), Byrne et al. (10), Schwenker and Beck (11), and others (12, 13, 14) involving the thermal decomposition of cellulose and analysis of the pyrolytic products, a major pathway for the decomposition of cellulose has been postulated. This involves depolymerization which requires scission of the 1,4-glycosidic carbon-oxygen bond. The resulting hexose unit then undergoes further reaction to yield one of the major pyrolytic products, 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan). It has also been postulated (10, 11) that levoglucosan undergoes further reaction during pyrolysis, leading to either repolymerization or fragmentation. Byrne et al. (10) have proposed that scission of the glycosidic bond does not necessarily lead to the formation of levoglucosan, contending that the initial hexose intermediate can undergo either further degradation or be the intermediate for levoglucosan formation. Kilzer and Broido (14) have proposed dehydration and decomposition as two additional competing pathways by which cellulose undergoes pyrolysis. The reaction products obtained from these dehydration reactions are the so-called "dehydrocelluloses" (14). The "dehydrocellulose" then undergoes decomposition to give additional volatile pyrolytic products. Byrne et al. (10) have shown that borate salts, added to cellulose at a 4.2% (w/w) level, completely inhibit the formation of levoglucosan when the pyrolysis was carried out at 420° C. Thermal analytical techniques also have been used to study the effect of borate salts on the decomposition of cellulose. Using thermogravimetric analyses (TGA), Tang and co-workers (15) found that between 220° and 360° C borate-treated cellulose undergoes less weight loss than untreated cellulose. Derivative thermogravimetric analysis (DTGA) curves of untreated and borate-treated cellulose used in this study are shown in Figure 7. These DTGA curves are in close agreement with those obtained by Tang, even though the latter were obtained in a nitrogen atmosphere. These curves show that the maximum rate of weight loss at 310° C for borate-treated cellulose is less than that for untreated cellulose. Also, the total weight loss, corrected for residual additive, of the borate-treated cellulose between 250° and 350° C is approximately 20% less than that from the untreated cellulose. Even though the maximum rate of change is decreased, the temperature at which these maxima occur is the same for both treated and untreated cellulose. This indicates

that borate is suppressing only the extent of volatilization below 350° C. However, at a temperature of 700° C, the total weight losses of borate-treated cellulose (adjusted for the weight of residual additive) and untreated cellulose are the same. This shows that the addition of borate has modified the mode of formation of volatile products, but not the extent of the formation of these products. The implication is not being made that the products will be qualitatively or quantitatively the same for cellulose and treated cellulose.

The decreased weight loss at low temperatures and the increased weight loss at high temperatures shown by the TGA of borate-treated cellulose as compared with cellulose, parallels the TGA data that have been obtained for borate-treated tobacco (5). This decrease in the weight loss of borate-treated tobacco at lower temperatures may be attributed, at least in part, to the effect of borate on the decomposition of the total carbohydrate present in the tobacco.

The foregoing thermal analytical data and the data of Byrne et al. (10) and Heyn and Klier (16) along with the knowledge that borate salts complex with carbohydrates in aqueous solution (17) indicate that borate forms a complex with the cellulose, which on pyrolysis yields no levoglucosan, and decreases the amount of volatile products formed at temperatures lower than 350° C. Because of this decrease in volatilization at lower temperatures, the formation of volatile products is increased at higher temperatures. This is evidenced by the same total weight losses for treated and untreated cellulose. Thus, it can be inferred that the borate complexes enhance the formation of nonvolatile "dehydrocellulose" which undergoes decomposition at higher temperatures. This postulation is supported by the work of Heyn (16) who found that the addition of borate to glucose increased the yield of unsaturated compounds, such as the substituted furans, and slightly decreased the yield of carbonyl compounds. He attributed the increased furan levels to the borate enhancing the polymerization of glucose. Also, that some of the substituted furans, by virtue of their structures, must be derived from the degradation of this polymerized glucose. From the data which have been discussed it can be inferred that the ability of borate salts to complex with carbohydrates plays a major role in increasing the yield of phenol from cellulose.

## 2. Cresols from Cellulose

The temperature-yield profiles of the cresols from cellulose (Figures 2 and 3) all have maxima at approximately 600° C. The temperature-yield profiles for o-cresol and m,p-cresol from borate-treated cellulose show that borate salts suppress the recovery of the cresols. Even though there are decreases in their yields there is no change in the temperature of maximum recovery. This decrease in the recovery is in contrast to the increased level of phenol and cresols from the isothermal pyrolysis of tobacco. It can be inferred from these comparisons that phenol and the cresols are not formed via the same pyrolytic intermediates or pathways.

Figure 2 Temperature-yield profile of o-cresol from cellulose  
Untreated — and borate-treated ----

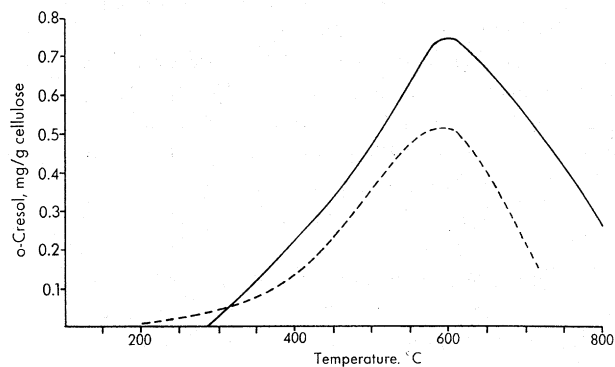
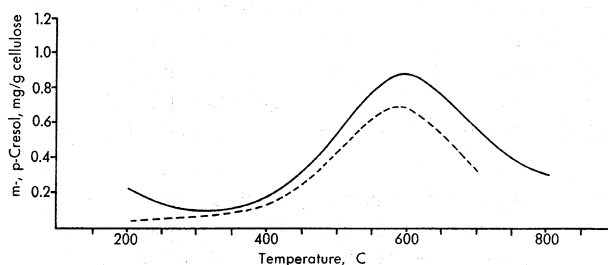


Figure 3 Temperature-yield profile for m-, p-cresol from cellulose  
Untreated — and borate-treated ----



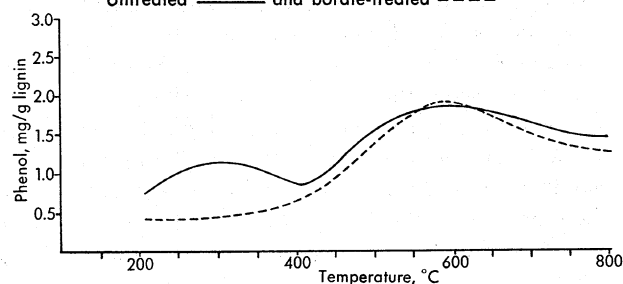
## 3. Phenol from Lignin

The temperature-yield profile of phenol from tobacco lignin is shown in Figure 4. This profile has two maxima, at 300° and 600° C, and is qualitatively similar to that obtained from untreated tobacco (2). Schlotzhauer et al. (18) obtained a curve of the total phenol recovery from the isothermal pyrolysis of wood lignin in both air and nitrogen.

Since these workers plotted the weight of the total phenolic residue, their values are much greater than the sum of the phenol and cresol values reported in this work. The temperature of the second maximum for the phenol recovery and the maxima for the cresol recoveries obtained in this work, however, do correspond to the maximum reported by Schlotzhauer for the pyrolysis in air. The temperature-yield profile for phenol from borate-treated lignin contains only one maximum at approximately 600° C, and shows no increase in the phenol recovery. Suppression of the low temperature maximum is qualitatively similar to that obtained from borate-treated tobacco.

These data from the temperature-yield profiles of phenol from lignin and borate-treated lignin give some

Figure 4 Temperature-yield profile for phenol from lignin  
Untreated — and borate-treated ----



insight to the general mode of decomposition of tobacco lignin. Since the profile of phenol from lignin contains two maxima it is apparent that phenol is formed via two synthetic pathways or intermediates. The low temperature maximum may be due to the decomposition of a phenol precursor which is a simple phenol derivative. It is difficult to conceive that phenol would be formed from polyphenolic moieties within the lignin structure, such as guaiacol, at temperatures as low as 300° C, since this would involve the scission of a phenolic oxygen. However, less highly substituted phenols present in the lignin structure, such as p-coumaryl alcohol and glucocoumaryl alcohol, are compounds of the type which may serve as precursors for phenols at low temperatures. Since borate salts suppress phenol recovery at lower temperatures, it is probable that they form complexes with such phenol precursors, thereby inhibiting phenol formation. This postulate is reasonable since lignin contains a large number of hydroxyl groups, many of which should be of the proper spatial orientation for complexation with borate (17).

Thermal analytical data obtained from untreated and borate-treated lignin also indicate that some form of complexation is involved. The DTGA of lignin, Figure 8, contains two maxima at lower temperatures, occurring at approximately 230° and 290° C. It is also apparent that there is a significant weight loss due to the decomposition of lignin at low temperatures. The TGA of borate-treated lignin show that borate salts suppress the maximum rate of weight change of lignin that occurs at 230° C. Therefore, borate salts, do indeed, inhibit the formation of volatile products at lower temperatures. This inhibition again gives support to the postulate that the borate salts are forming a complex with specific phenol precursors in lignin, thereby inhibiting phenol formation at the lower temperatures.

Since the temperature-yield profiles show that there are no differences between the phenol recoveries from lignin and borate-treated lignin at higher temperatures, it is apparent that at these temperatures borate has no major effect on the phenol recovery. Therefore, phenol recovery at higher temperatures is independent of any effects that borate salts might have. This indicates that any complexes between borate salts and lignin are thermally labile and are probably broken at approximately 400° C.

Data obtained for the yields of phenol from lignin and borate-treated lignin agree with the data obtained from untreated and borate-treated tobacco. There is good agreement between the suppression of the low temperature maximum at 300° C for tobacco and tobacco lignin. It should be noted that on a mg/g basis the yield of phenol from lignin and tobacco are approximately the same. Since the lignin content of tobacco is generally less than approximately 3.5 %, lignin would make only a small contribution to the total yield of phenol obtained from tobacco at the lower temperatures. Therefore, the low temperature maximum of phenol recovery from tobacco cannot be attributed solely to lignin.

Figure 5 Temperature-yield profile for o-cresol from lignin  
Untreated — and borate-treated ----

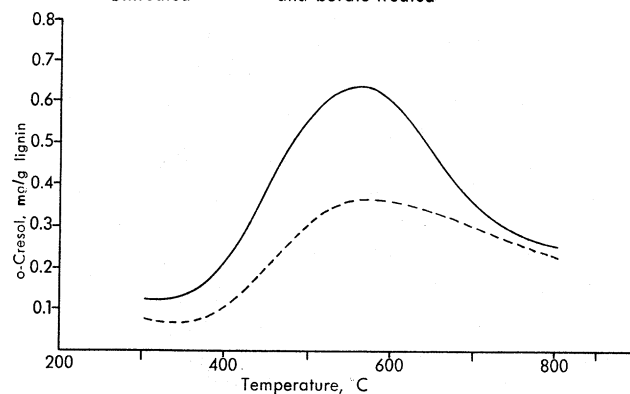
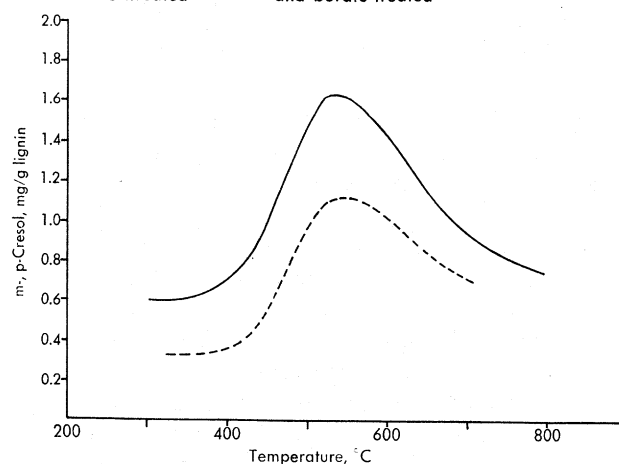


Figure 6 Temperature-yield profile of m-, p-cresol from lignin  
Untreated — and borate-treated ----



Consequently, for borate-treated tobacco the suppression of this low temperature maximum should not be attributed to the action of the borate salts on lignin.

#### 4. Cresols from Lignin

The temperature-yield profiles of the cresols from lignin (Figures 5 and 6) vary little from those for the cresols from cellulose. They have a maximum temperature of recovery at 600° C. The ratio of o-cresol to m-, p-cresol is approximately 1:2.5. Addition of borate to lignin influences the temperature-yield profile very little except that the recoveries are less than those from untreated lignin. This is contrary to the data obtained from tobacco (2) where borate salts enhance the yield of the cresols. Therefore, it can be inferred that borate-treated lignin, as with cellulose, is not contributing to the increase of cresols obtained from the treated tobacco, but rather it should have a small negative effect.

#### SUMMARY

The data obtained from the isothermal pyrolysis of untreated and borate-treated cellulose and lignin show that borate salts influence the yields of phenol, o-cresol, and m-p-cresol from these two tobacco leaf constituents. The observed differences between the level of phenol from tobacco and borate-treated tobacco can be at least partially attributed to the effect of borate salts

on the pyrolysis of lignin and cellulose. It must be emphasized, however, that the contribution of cellulose and lignin to the formation of phenol and cresols obtained from the pyrolysis of tobacco should not be quantitatively compared with the level of phenol and cresols obtained from the pyrolysis of pure cellulose and lignin. This is also true of borate-treated cellulose and borate-treated lignin. The main conclusion from this study is that borate salts do affect the recovery of phenol and cresols from leaf constituents such as lignin and cellulose and may be partially responsible for the increased levels of phenol obtained from the isothermal pyrolysis of borate-treated tobacco.

## ZUSAMMENFASSUNG

Die Ergebnisse, die bei der isothermen Pyrolyse von unbehandelter und mit Borat behandelter Cellulose und unbehandeltem und mit Borat behandeltem Lignin erhalten werden, zeigen, daß Borsalze die Ausbeuten an Phenol, an o-Kresol und m-, p-Kresol aus den beiden Tabakblattbestandteilen beeinflussen. Die beobachteten Unterschiede zwischen der Ausbeute an Phenol aus Tabak und mit Borat behandeltem Tabak können zumindest teilweise auf den Einfluß von Borsalzen auf die Pyrolyse von Lignin und Cellulose zurückgeführt werden. Es muß betont werden, daß der Beitrag von Cellulose und Lignin an der Bildung von Phenol und Kresolen bei der Pyrolyse von Tabak nicht quantitativ verglichen werden darf mit den Anteilen an Phenol und Kresolen, die bei der Pyrolyse von reiner Cellulose und reinem Lignin erhalten werden. Das gilt auch für mit Borat behandelte Cellulose und mit Borat behandeltes Lignin. Der Hauptschluß aus dieser Arbeit ist, daß Borsalze das Entstehen von Phenol und Kresolen aus Blattbestandteilen wie Lignin und Cellulose beeinflussen und vielleicht teilweise verantwortlich sind für die gestiegenen Anteile an Phenol, die bei der isothermen Pyrolyse von mit Borat behandeltem Tabak erhalten werden.

## RÉSUMÉ

Les valeurs obtenues par pyrolyse isotherme de la cellulose et de la lignine traitées au borate ou non traitées montrent que les borates influencent les rendements en phénol, o-crésol et m-,p-crésol de ces deux constituants de la feuille de tabac. Les différences observées entre les rendements en phénols du tabac suivant qu'il est ou non traité au borate peuvent être, au moins partiellement, attribuées à l'effet des borates sur la pyrolyse de la lignine et de la cellulose. On doit préciser, toutefois, que la contribution de la cellulose et de la lignine à la formation du phénol et des crésols obtenus par pyrolyse du tabac ne devrait pas être comparée quantitativement au taux des phénols et crésols obtenus par pyrolyse de la cellulose et de la lignine pures. C'est également vrai pour la cellulose et la lignine traitées au borate. La principale conclusion de cette étude est que les borates influent sur les quantités de phénol et crésols obtenus

Figure 7 Thermogravimetric (upper) and differential thermogravimetric (lower) curves

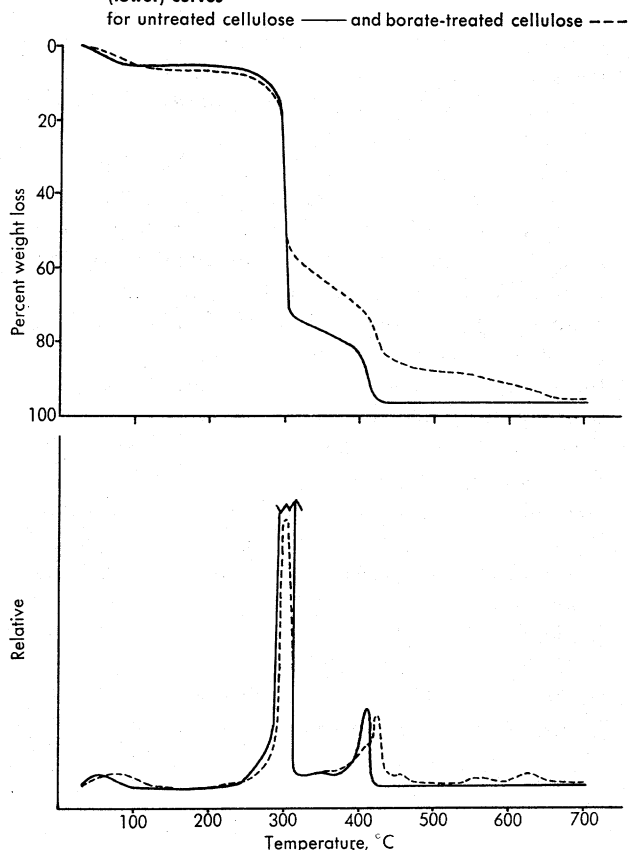
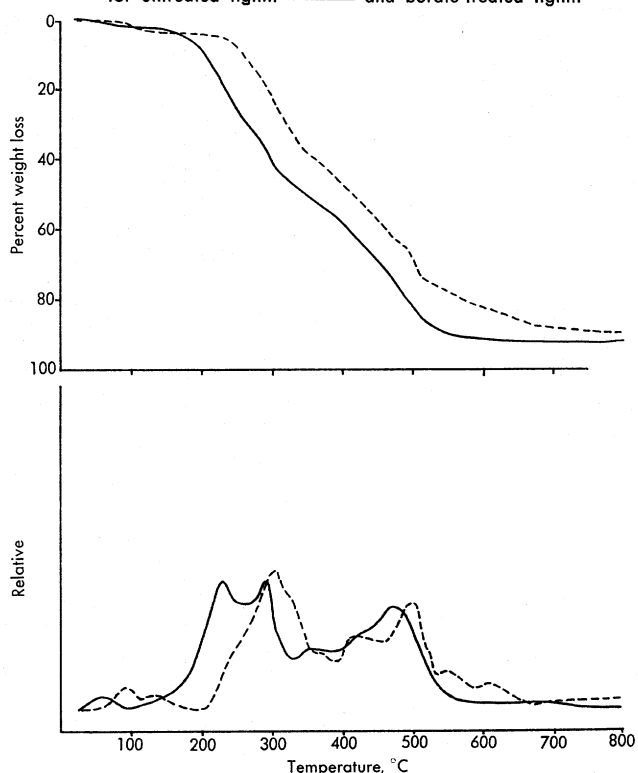


Figure 8 Thermogravimetric (upper) and differential thermogravimetric (lower) curves for untreated lignin — and borate-treated lignin ---



des constituants de la feuille tels que la cellulose et la lignine, et peuvent être partiellement responsables de l'accroissement des taux de phénol obtenus par pyrolyse isotherme du tabac traité au borate.

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